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Physics Procedia 9 (2010) 49–53

Physics Procedia

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12th International Conference on Magnetic Fluids

The role of van der Waals forces in ferrofluid phase separation

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Abstract

The phase separation conditions of sterically stabilized ferrofluids are studied theoretically with major attention paid to the roles of polydispersity and van der Waals attraction. The equilibrium phase stability region is completely determined by a small number of large particles. Highly concentrated drop-like aggregates formed upon separation take up several percent of the volume of a system and account for virtually all of the large-particle fraction. Our analysis also demonstrates that van der Waals interactions play a significant role in ferrofluid phase separation; their influence is comparable to that of dipolar forces.

Keywords: magnetic fluid; van der Waals attraction; phase separation

1. Introduction

The phenomenon of magnetic fluid phase separation, accompanied by the formation of drop-like aggregates, was first observed over thirty years ago [1]. These aggregates can be considered as fluids with an interfacial tension surface, representing, essentially, a highly concentrated ferrofluid phase, suspended in a dilute matrix in the form of droplets. Typical dimensions of the drop-like aggregates are on the order of about 1-5 μm, i.e., the number of ferroparticles within the aggregate is approximately 10^4-10^6. Later this phenomenon was thoroughly studied experimentally [2], and three major factors which can lead to phase separation were revealed: (a) a decrease in temperature; (b) a strengthening of an applied magnetic field; and (c) an increase of the solvent ionic strength for ionic ferrofluids.

Conventional theoretical models [3] have demonstrated that, in principle, a system of particles interacting through a non-central dipole-dipole potential may undergo condensation even in the absence of a magnetic field, at a temperature below a certain critical value which depends on the value of particle magnetic moment. This is associated with the fact that the non-central magnetic dipole-dipole interaction of ferroparticles manifests itself as an effective interparticle attraction. In an external field this effective attraction is enhanced; thus, a magnetic field stimulates the process of phase separation in ferrofluids. But the problem is that in computer simulations of dipolar fluids with hard or soft spheres no condensation transition has been observed [4]. Only when the van der Waals

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1875-3892
doi:10.1016/j.phpro.2010.11.013

attraction is added to the magnetic dipolar interaction can the phase transition be found (as in Stockmayer fluids [5]). So, the question is: what is the driving force for the phase separation in real ferrofluids? Is it really influenced by the dipolar interaction only? And what is the role of the van der Waals attraction in the phase separation of ferrofluids?

2. Theory

To answer these questions we examine first the van der Waals interaction in a system of identical spherical ferroparticles coated by a surfactant layer of thickness l:

$$U_w(r) = -\frac{A}{12}\left(\frac{d^2}{r^2} + \frac{d^2}{r^2 - d^2} + 2\ln\frac{r^2 - d^2}{r^2}\right). \qquad (1)$$

Here A is the Hamaker constant, r stands for the particle center-to-center distance, and d is the diameter of the solid particle/grain. For typical parameters d=10nm and l=2nm we obtain the approximate contact value

$$U_w(r = d + 2l) \approx 0.01A\,. \qquad (2)$$

For ferrite colloids in hydrocarbons ($A \approx 3\times10^{-19}$J) it means that the contact van der Waals energy at room temperature is comparable to the thermal energy $kT \approx 4\times10^{-21}$J. At the same time, the commonly used long-range approximation to expression (1)

$$U_w(r) \approx -\frac{A}{36}\left(\frac{d}{r}\right)^6, \qquad (3)$$

gives the contact value

$$U_w(r = d + 2l) \approx 0.0037A, \qquad (4)$$

which is three times smaller than the real one (2). This estimation shows that the van der Waals energy should not be neglected when we describe the conditions of ferrofluid phase separation.

Next we develop a simple model based on the thermodynamic perturbation method. The main advantage of this model is that it may easily be extended to the case of polydisperse ferrofluids as well as to various kinds of central interparticle interaction. The test of the model on Stockmayer fluids results in a rather accurate description of the critical point and the phase diagram. The comparison for the reduced critical temperature $T_c^* = kT_c / \varepsilon_{LJ}$ is presented in Table 1 for various values of the reduced magnetic moment $\mu = m / \sqrt{d^3 \varepsilon_{LJ}}$ and the reduced magnetic field $H^* = H\sqrt{d^3 / \varepsilon_{LJ}}$, where ε_{LJ} is the depth of a potential minimum.

3. Results

The model is now applied to a theoretical investigation of the phase separation conditions in a ferrofluid, the particles of which are considered with the help of "core-shell" model. Each particle consists of a homogeneously magnetized core of diameter x, and a surrounding shell made up of a non-magnetic surface metallic layer (width δ) and a surfactant layer (width l). The particle magnetic moment m is proportional to the volume of the magnetic grain. The whole width of the shell is $l+\delta$, and we assume that the surfactant layers are very rigid. So, the external "hydrodynamic" diameter d of the ferroparticle is $d=x+2l+2\delta$. The particles interact via the hard sphere repulsion, the van der Waals attraction, and the magnetic dipole-dipole interaction. The intensity of the magnetic interaction is measured with the dipolar coupling constant $\lambda = m^2/d^3kT$.

Table 1. Reduced critical temperature T^*_c for the Stockmayer fluid for various values of the reduced magnetic moment μ and reduced magnetic field H^*.

μ	H^*	T^*_c computer simulation [5]	T^*_c model
0	0	1.316(6)	1.306
1	0	1.41(1)	1.409
1	1	1.44(1)	1.428
1	2	1.49(1)	1.471
1	3	1.51(1)	1.517
$\sqrt{2}$	0	1.60(1)	1.669
$\sqrt{3}$	0	1.82(1)	2.016

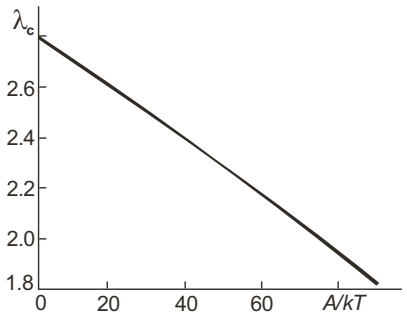

Fig. 1. Dependence of the critical value of the dipolar coupling constant λ_c on the relative energy of the van der Waals attraction A/kT for zero magnetic field.

The dependence of the critical dipolar coupling constant λ_c (inversely proportional to the critical temperature) on the relative energy of the van der Waals attraction A/kT is shown in Fig. 1 for zero magnetic field. In the framework of the present thermodynamic model, first described in Ref. [6], the neglect of van der Waals forces gives a critical dipolar coupling constant of approximately $\lambda_c \approx 2.8$, and the critical volume fraction appears to be $\varphi_c = \pi n_c d^3/6 = 0.130$ (here n_c stands for the critical number density). The value of $\lambda_c \approx 2.8$ is close to the region of chain aggregate formation, and for real magnetite ferrofluids it corresponds to diameters of the magnetic grains of $x \approx 20$-22nm. Real ferrofluids do not contain sufficient numbers of such large particles to drive purely dipolar condensation. But with proper account of the van der Waals interaction, we find the critical dipolar coupling constant to be $\lambda_c \approx 1.8$-2.0 (for $A/kT \approx 70$-80 at room temperature). This critical value corresponds to the large-particle fraction in ferrofluids, with realistic magnetic-grain diameters of $x \approx 15$-16nm.

An external magnetic field stimulates the effective dipole interparticle attraction and thus induces the phase separation. The critical dipolar coupling constant decreases monotonically with increasing external field.

4. Bidisperse ferrofluids

The next step is the investigation of the phase separation conditions including the influence of ferroparticle polydispersity. We use here the bidisperse model, in which the ferrofluid is considered as a binary colloidal system consisting of a large number of small particles with diameter x_1, and a small number of rather large particles with diameter x_2. Two systems are considered: in system I we choose x_1=8 nm and x_2=15 nm; in system II, x_1=7 nm and x_2=16 nm. In both systems the mole fraction of large particles is only 5%. In addition to Ref. [6] we study here the influence of the non-magnetic surface metallic layer δ on the phase diagram for the model bidisperse ferrofluids. These diagrams are presented in Fig. 2 for various δ.

In system I we could only observe the phase separation at room temperatures in rather strong magnetic fields (~10kA/m). The phase-stability curve for system II is shifted towards the right by 60K; this ferrofluid undergoes phase separation in zero magnetic field even at room temperatures. We should point out that such a large shift results from only a 1nm increase in the large-particle diameter. The physical reason is obvious; the volume of the large-particle magnetic grains in system II exceeds that in system I by 20%. Hence, the intensity of the interparticle magnetic attraction is higher in system II, and this attraction leads to the phase separation at higher temperatures.

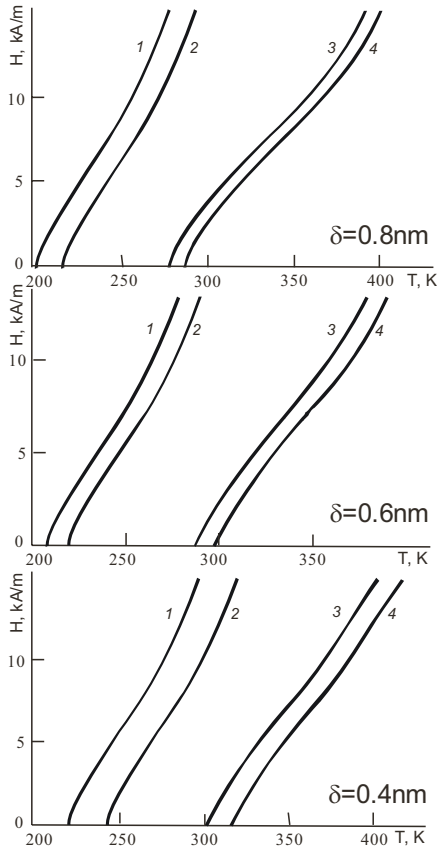

Fig. 2. Phase diagram for the model bidisperse ferrofluids in the plane: temperature – magnetic field strength. Curve 1 corresponds to the system I, curve 2 – the system II, curve 3 - the system I without van der Waals, curve 4 - the system II without van der Waals. For each curve the upper region is the separated two-phase state.

5. Conclusions

The equilibrium phase stability region is completely determined by a small number of large particles. Highly concentrated drop-like aggregates formed upon separation take up several percent of the volume of the system and include virtually the entire large-particle fraction. Our analysis demonstrates that van der Waals interactions play a significant role in ferrofluid phase separation; their influence is comparable with that of dipolar forces.

Acknowledgments

This research was carried out within the partial financial support of RFBR Grant No. 08-02-00647, FAE Pr. № 2.1.1/1535, FASI Pr. No. 02.740.11.0202, Grant of the President of RF № MK-1673.2010.2.

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